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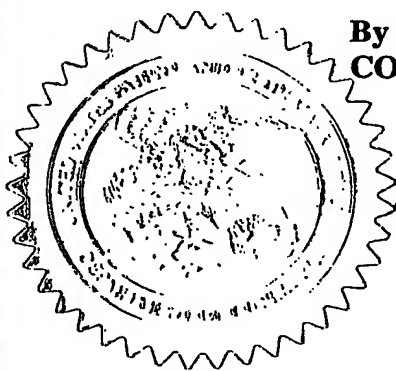
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JC693 U.S. PTO

01-15-980439912.011302 A/PK

Practitioner's Docket No. 100325.0199PRO

PATENT

Preliminary Classification  
Proposed Class:  
Subclass:

Jc612 U.S. PTO  
60/439912  
01/13/03

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Ashok Rao and Keith Stroehler

For: Improved Configurations and Process for Shift Conversion

Box Provisional Patent Application  
Commissioner for Patents  
Washington, D.C. 20231

COVER SHEET FOR FILING PROVISIONAL APPLICATION  
(37 C.F.R. § 1.51(c)(1))

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i). The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):
2. The names of the inventors are (37 C.F.R. § 1.51(c)(1)(ii)):
  1. Ashok Rao
  2. Keith Stroehler

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3. Residence addresses of the inventors, as numbered above (37 C.F.R. § 1.51(c)(1)(iii)):

1. 50 Segada  
Rancho Santa Margarita, CA 92688
2. 2 Enterprise Dr. #3202  
Aliso Viejo, CA 92656

4. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

Improved Configurations and Process for Shift Conversion

5. The name, registration, customer and telephone numbers of the practitioner are (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: Martin Fessenmaier  
Reg. No. 46697  
Tel. 714-641-5100  
Customer No. 34284

6. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No. 100325.0199PRO

7. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

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611 Anton Blvd., Suite 1400  
P.O. Box 1950  
Costa Mesa, CA 92626

8. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was NOT made by an agency of the United States Government, or under contract with an agency of the United States Government.

9. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. § 1.51(c)(2)-(3):

Specification:	No. of pages	6
Drawings:	No. of sheets	3

B. Additional documents:

Claims:	No. of claims	8
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10. Fee

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11. Fee payment

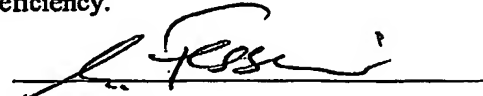
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Date: 01/13/03



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## IMPROVED CONFIGURATION AND PROCESS FOR SHIFT CONVERSION

### Field of The Invention

The field of the invention is hydrogen production, and especially relates to configurations and processes that reduce steam consumption in hydrogen production from synthesis gas while  
5 maintaining a certain design value for the hydrogen to carbon monoxide ratio.

### Background of The Invention

Numerous processes are known in the art to produce hydrogen from various materials, including steam reforming of natural gas, syngas, or naphtha, catalytic reforming of heavy straight run gasoline or heavy oils (*e.g.*, fuel oil), and partial oxidation of heavy oils or natural  
10 gas. Steam reforming of hydrocarbonaceous material is particularly advantageous due to the relatively simple configuration and relatively robust operation. However, generation of steam for the reforming process requires often relatively large quantities of energy.

To reduce the energy demand for steam production, steam may be internally provided by quenching hot gas from the reformer in direct contact with water as described in U.S. Pat. No.  
15 3,545,926 to Schlinger et al., or in U.S. Pat. No. 5,152,975 to Fong et al. Such configurations may provide a significant reduction in energy consumption for steam production. However, depending on the particular operating conditions, it may be necessary to heat the quenched gas prior to entry into the shift converter, which reduces the energy savings to at least some degree.

Alternatively, the reforming process may be split into two sections in which the feed gas  
20 is reformed with steam in the first section and with oxygen in the second section as described in U.S. Pat. No. 4,782,096 to Banquy. While such configurations generally require less overall steam as compared to a conventional steam reforming processes, several disadvantages nevertheless remain. Among other things, operation of the second section generally requires an oxygen rich gas (typically comprising 80 vol% or even more oxygen), which has to be generated  
25 in an air separation or other oxygen enrichment equipment.

Therefore, while various configurations and methods to reduce energy costs associated with steam generation are known in the art of steam reforming, all or almost all of them suffer from one or more disadvantages. Thus, there is still a need to provide improved configurations

and methods to reduce energy costs associated with steam consumption in steam reforming, partial oxidation and gasification plants.

### **Brief Description of The Drawing**

Figure 1A is a schematic of an exemplary configuration for hydrogen production from synthesis gas according to the inventive subject matter.

Figure 1B is a table indicating composition, flow rate, and temperature of various streams of the configuration of Figure 1A.

Figure 2A is a prior art schematic of a known configuration for hydrogen production from synthesis gas.

Figure 2B is a table indicating composition, flow rate, and temperature of various streams of the configuration of Figure 2A.

### **Detailed Description**

In most currently known configurations for production of hydrogen from synthesis gas (and particularly from synthesis gas with high carbon monoxide to hydrogen ratio), steam is required in quantities far in excess of the amount required by stoichiometry for the shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ ) is required. The inventors unexpectedly discovered that the excess steam predominantly serves to limit the temperature rise across the catalytic reactor, as the reforming reaction is highly exothermic. Consequently, the inventors contemplate a process configuration in which a first fraction of the total feed gas is bypassed around a first shift reactor to reduce the amount of produced heat and thus to reduce the amount of required steam. A second fraction of the total feed gas is combined with the processed first fraction and then fed into a second shift reactor to complete the conversion of the total feed gas.

An exemplary contemplated configuration is depicted in Figure 1A in which a plant includes a shift conversion unit 100 having a first shift reactor 110 and a second shift reactor 120. Syngas stream 1 (or syngas stream 2 where a bypass is employed; see below) is split into a first feed stream and a second feed stream, wherein the first feed stream (about 40 vol% of total feed gas stream 1) is combined with steam 3 to form stream 4, and wherein the second feed

stream 9 (about 60 vol% of total feed gas stream 2) is bypassed around the first shift reactor 110. Stream 4 may be preheated by feed preheater 105 before entering the first shift reactor 110. The effluent 5 from the first shift reactor 110 is then cooled by effluent cooler 115, and the cooled effluent 5 is combined with the second feed stream 9 to form mixed feed stream 6 that is then fed  
5 to the second shift reactor 120. The effluent 7 from the second shift reactor 120 may then be combined with bypass stream 10 (which may be drawn from the syngas stream 1 to control conversion) to form hydrogen rich product stream 8. Exemplary calculated composition, flow rate, and temperature of various streams as indicated above and in Figure 1A are shown in the table of Figure 1B.

10 For comparison, **Prior Art Figure 2A** depicts a typical steam shift configuration 200 in which a first steam reactor 210 and a second steam reactor 220 provide conversion of a syngas stream 1 to a hydrogen rich product stream 8 with the same amount of CO shifted to H<sub>2</sub> as the previous case (*i.e.*, same H<sub>2</sub> to CO ratio in the product stream leaving the shift unit). More particularly, syngas stream 1 is divided into syngas stream 2 (typically about 83 vol% of syngas  
15 stream 1) and bypass stream 9 (typically about 17 vol% of syngas stream 1). The syngas stream 2 is combined with steam 3 to form stream 4, which is preheated by feed preheater 205 before entering the first shift reactor 210. The effluent 5 from the first shift reactor 210 is then cooled by effluent cooler 215 to stream 6 that is fed to the second shift reactor 220. The effluent 7 from the second shift reactor 220 is combined with bypass stream 9 (to control conversion) to form  
20 hydrogen rich product stream 8. Exemplary calculated composition, flow rate, and temperature of various streams as indicated above and in Figure 2A are shown in the table of Figure 2B.

Therefore, the inventors generally contemplate a plant comprising a first shift reactor and a second shift reactor, wherein the first shift reactor receives a first portion of a feed gas to form a processed feed gas, and wherein the processed feed gas is combined with a second portion of  
25 the feed gas to form a mixed feed gas that is fed to the second shift reactor, thereby reducing steam consumption of a reforming process of the feed gas. Particularly preferred feed gases include syngas from a gasification reactor or partial oxidation unit, and it is especially preferred that the first portion of the feed gas is between 50 vol% to about 75 vol% of the feed gas. In yet further contemplated aspects, suitable plants may further comprise a bypass that combines part of  
30 the feed gas with an effluent gas from the second shift reactor to control the conversion.

The nature, composition and pressure of suitable feed gases may vary considerably and it should be recognized that all feed gases with a significant amount of carbon monoxide are considered appropriate. However, it is especially preferred that the feed gas is a syngas from a gasification plant or partial oxidation unit. Thus, particularly preferred feed gases will typically have a carbon monoxide to hydrogen ratio in excess of 2 (a typical syn gas may comprise 50 mol% carbon monoxide, and 20 mol% hydrogen, with the balance including nitrogen, carbon dioxide, sulfurous compounds, and inert gases). With respect to the shift reactors, it should be recognized that all known types and sizes may be used in conjunction with the configuration according to the inventive subject matter. Similarly, where a catalyst is employed, all known shift catalysts are deemed suitable for use herein.

It is further contemplated that the particular amount of feed gas that is bypassed around the first shift reactor may vary considerably, and generally contemplated amounts are between less than about 10 vol% and about 90 vol%, and even higher. However, with most typical operations, and depending on the composition of the syngas or other feed gas, and the required  $H_2$  to CO ratio in the product stream leaving the shift unit, the amount of feed gas that is bypassed around the first shift reactor may be between about 50 vol% to about 75 vol%. Similarly, the amount of bypass to control the conversion may vary considerably, and typical amounts will generally lie between zero and about 25 vol%.

Based on calculations using configurations according to Figures 1A and 2A, the inventors determined that by bypassing a portion of the syngas around the first shift reactor, the steam consumption can be reduced by as much as 50 to 60 percent. However, it should be appreciated that the particular savings will depend to at least some degree on the carbon monoxide/hydrogen ratio of the feed gas. The so saved steam may then be utilized for other processes, and especially for the generation of power. For example, in a commercial sized power plant (total equivalent power capacity of 400 MW), the calculated power that may be generated from the saved steam is in excess of 50 MW.

In a particularly contemplated aspect of the inventive subject matter, it should be recognized that configurations and methods according to the inventive subject matter are especially suitable for plants in which deep carbon monoxide conversion is not required. For

example, suitable plants include those that coproduce a fuel gas that may be supplied to a gas turbine or fuel cell and/or a fired equipment (*e.g.*, furnace or boiler), wherein the high purity hydrogen for such plants is provided via membranes and/or a pressure swing adsorption unit that purifies the shifted gas.

5           Alternatively, contemplated methods and configurations may be employed as retrofit in various petrochemical plants that consume hydrogen that is currently generated from natural gas. Replacement of such hydrogen production with hydrogen production from gasification of alternative fuels (*e.g.*, refinery residues or coal) may be especially advantageous in view of environmental as well as economical aspects. Among other things, penalties for carbon dioxide  
10          emission may be reduced using contemplated configurations in which hydrogen is produced from syngas generated from coal or other cheap fuel and combusted in the gas turbine of a combined cycle, while the carbon dioxide is separated from the shifted gas and sequestered.

          In another example, contemplated configurations and methods may become increasingly attractive to crude oil refineries as the quality of crude oil decreases with a concomitant increase  
15          in low quality heavy residues (*e.g.*, heavy oils or coke) production, which may be consumed within the refinery using hydrogen (*e.g.*, via hydrogenation and/or hydrocracking) generated by configurations and methods presented herein. In still further examples, contemplated configurations and methods may be employed in synthesis plants (*e.g.*, plants producing methanol, dimethyl ether, Fischer Tropsch liquids, etc.) that require adjustment of the carbon  
20          monoxide to hydrogen ratio in the feed gas.

          It should still further be recognized that contemplated configurations and methods will advantageously reduce the size of the shift reactor(s), significantly reduce steam usage which results in more steam being available for other purposes (*e.g.*, power generation or reduction of fuel usage if the steam is generated in a fired boiler), minimize the amount of condensate  
25          generated when the shifted gas is cooled for further processing, handling/treatment, and reduce the size of equipment used to cool the shifted gas.

          Therefore, the inventors contemplate a method of reducing steam consumption in a shift conversion processes, in which in one step a first shift reactor and a second shift reactor are provided. In another step, feed gas is separated into a first portion and a second portion, wherein

the first portion is fed to the first shift reactor to produce a processed feed gas. In yet another step, the processed feed gas is combined with the second portion to form a mixed feed gas, and in still another step, the mixed feed gas is fed to the second shift reactor. It should also be noted that the disclosed process configuration is not limited to two-reactor systems. For example, a series of three or more reactors may be utilized in which the gas by-passed around one reactor is fed to a reactor downstream the one reactor.

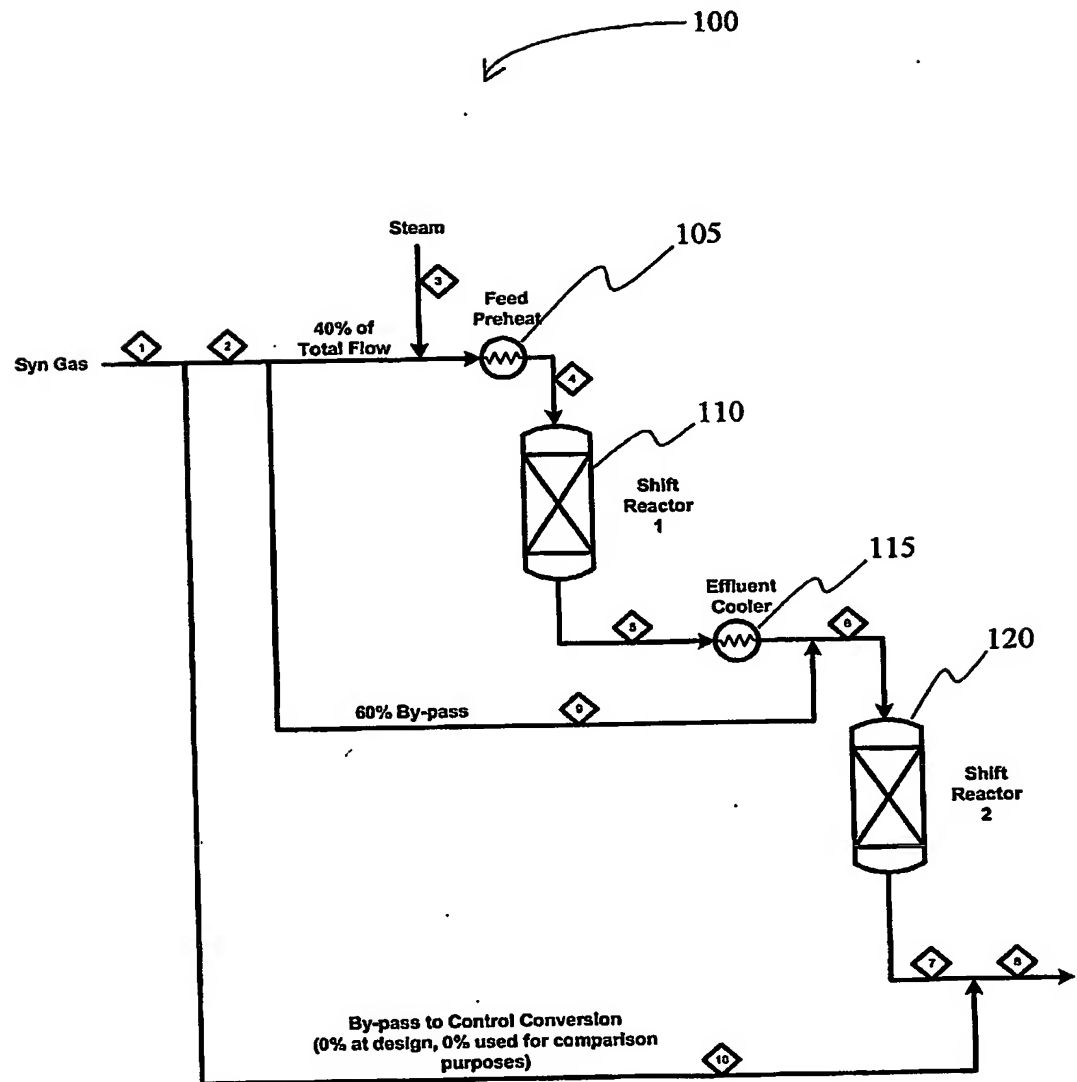
Thus, specific embodiments and applications of improved configurations and processes for a shift reaction have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the appended contemplated claims. Moreover, in interpreting both the specification and the contemplated claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.

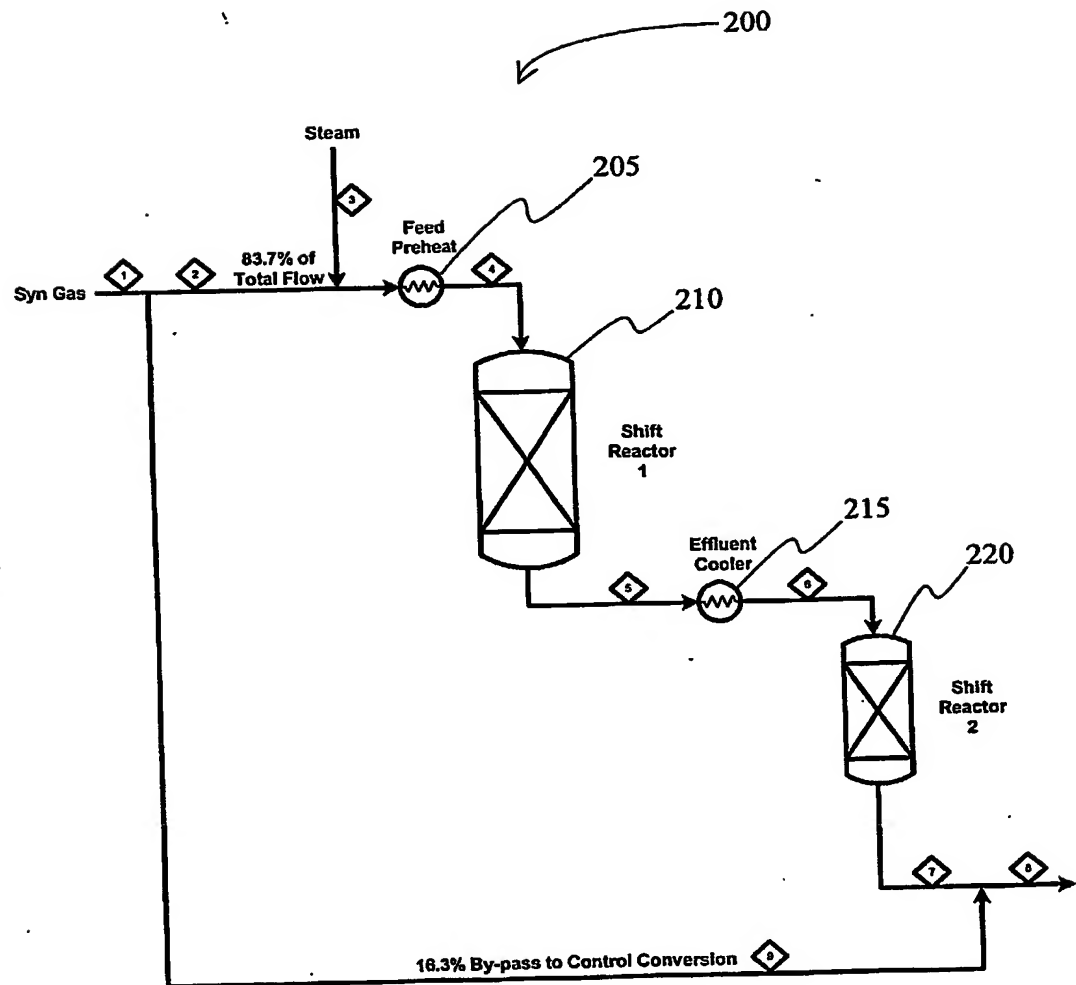
**CONTEMPLATED CLAIMS**

The following claims are provided to add additional clarity to this disclosure. Future applications claiming priority to this application may or may not include the following claims, and may include claims broader, narrower, or entirely different from the following claims.

- 5 1. A plant comprising a first shift reactor and a second shift reactor, wherein the first shift reactor receives a first portion of a feed gas to form a processed feed gas, and wherein the processed feed gas is combined with a second portion of the feed gas to form a mixed feed gas that is fed to the second shift reactor, thereby reducing steam consumption of a carbon monoxide shifting process of the feed gas.
- 10 2. The plant of claim 1 wherein the feed gas comprises a syngas from a gasification unit or a partial oxidation unit.
3. The plant of claim 1 wherein the first portion of the feed gas is between 50 vol% to about 75 vol% of the feed gas.
4. The plant of claim 1 further comprising a bypass that combines part of the feed gas with  
15 an effluent gas from the second shift reactor.
5. A method of reducing steam consumption comprising:  
  
providing a first shift reactor and a second shift reactor;  
  
separating a feed gas into a first portion and a second portion, and feeding the first  
portion to the first shift reactor to produce a processed feed gas;  
20 combining the processed feed gas with the second portion to form a mixed feed gas; and  
  
feeding the mixed feed gas to the second shift reactor.
6. The method of claim 5 wherein the feed gas comprises a syngas from a gasification unit or a partial oxidation unit.
7. The method of claim 5 wherein the first portion of the feed gas is between 50 vol% to  
25 about 75 vol% of the feed gas.

8. The method of claim 5 further comprising a bypass that combines part of the feed gas with an effluent gas from the second shift reactor.

**Figure 1A**



Prior Art Figure 2A

Stream #	1	2	3	4	5	6	7	8	9	10
Mole flow, lbmole/hr										
CO	22174	22174	0	8869	742	14046	3988	3988	13304	0
H2	11191	11191	0	4476	12604	19319	29378	29378	6715	0
CO2	554	554	0	222	8360	8693	18767	18767	333	0
CH4	13	13	0	5	5	13	13	13	8	0
AR	288	288	0	115	115	288	288	288	173	0
N2	2755	2755	0	1102	1102	2755	2755	2755	1653	0
O2	0	0	0	0	0	0	0	0	0	0
NH3	9	9	0	4	4	9	9	9	5	0
H2S	244	244	0	98	108	254	269	269	148	0
COS	27	27	0	11	0	16	1	1	18	0
H2O	7097	7097	30752	33591	25452	29710	19636	19636	4258	0
Total Flow lbmol/hr	44352	44352	30752	48492	48492	75103	75103	75103	26611	0
Total Flow lb/hr	894864	894864	554003	911949	911949	1448867	1448867	1448867	536918	0
Total Flow cuft/hr	649591	649591	545324	878848	1207737	1461817	1888994	1888994	389754	0
Temperature F	320	320	700	550	850	550	802	802	320	
Pressure psi	575	575	650	572	582	552	642	642	575	
Vapor Frac	1	1	1	1	1	1	1	1	1	

Figure 1B

Stream #	1	2	3	4	5	6	7	8	9
Mole flow, lbmol/hr									
CO	22174	18561	0	18561	1537	1537	374	3988	3612
H2	11191	9368	0	9368	26392	26392	27556	29379	1823
CO2	554	464	0	464	17510	17510	18674	18764	90
CH4	13	11	0	11	11	11	11	13	2
AR	288	241	0	241	241	241	241	288	47
N2	2755	2306	0	2306	2306	2306	2306	2755	449
O2	0	0	0	0	0	0	0	0	0
NH3	9	7	0	7	7	7	7	9	1
H2S	244	204	0	204	226	226	226	266	40
COS	27	22	0	22	0	0	0	4	4
H2O	7097	5941	64727	70688	53622	53622	52458	53614	1156
Total Flow lbmol/hr	44352	37126	84727	101853	101853	101853	101853	109079	7228
Total Flow lb/hr	894873	749087	1166070	1915157	1915157	1915157	1915157	2080943	145786
Total Flow cuft/hr	649597	543769	1147801	1845570	2534548	1947308	2030718	2147774	105828
Temperature F	320	320	700	550	849	550	570	556	320
Pressure psi	575	575	650	572	562	552	542	542	575
Vapor Frac	1	1	1	1	1	1	1	1	1

Prior Art Figure 2B

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